SELF-DIFFUSION COEFFICIENT

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1. Theory

The *self-diffusion coefficient* D can be calculated from Einstein relation as

$$D = \lim_{t\to\infty} \frac{\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle}{6t}, \tag{1}$$

where $\vec{r}(t)$ denotes vector position at time t.

The self-diffusion constant is a single-particle phenomenon so that one can improve the statistical precision of results by averaging over N particles in the system,

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle \frac{1}{N} \sum_{i=1}^{N} [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle. \tag{2}$$

2. Implementation

In realizing Eq. 2 from simulation, the brackets would be interpreted as averages over *time origins*

$$D = \lim_{t\to\infty} \frac{1}{6t} \left\{ \lim_{\tau\to\infty} \frac{1}{N\tau} \sum_{i=1}^{N} \int_0^{\tau} [\vec{r}_i(t_0+t) - \vec{r}_i(t_0)]^2 \, dt_0 \right\}. \tag{3}$$

In simulations, one uses discrete time steps, so that one has a set of discrete times $\{t_1, t_2, \ldots, t_{N_{tot}}\}$, where $t_i = t_0 + (i-1)\Delta t$ for $i = 1, 2, \ldots, N_{tot}$ and Δt is the *time step*. *Total time simulation* is given by $t_{simul} = t_{N_{tot}} - t_1$. Time origins belong to set of discrete times $\{t_1, t_2, \ldots, t_{N_{or}}\}$, where $N_{or} = \frac{N_{tot}}{2}$. *Elapsed time* is set equal to $t = n\Delta t$, where $n = 1, 2, \ldots, N_{or}$. Thus,

$$D = \lim_{t\to\infty} D(t), \tag{4}$$

where

$$D(t) = \frac{1}{6t}\frac{1}{NN_{or}}\sum_{i=1}^{N}\sum_{j=1}^{N_{or}}\left[\vec{r}_i(t_j+t)-\vec{r}_i(t_j)\right]^2 . \tag{5}$$